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Esterification of levulinic acid with 1-butene over acidic ion-exchange resins: Operating conditions and thermodynamic study.

Esterificación de ácido levulínico con 1-buteno sobre resinas ácidas de intercambio iónico: condiciones de operación y estudio termodinámico.

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El mundo que hemos creado es un proceso de nuestro pensamiento. No se puede cambiar sin cambiar nuestra forma de pensar.

Albert Einstein

A mi familia y amigos por todo el apoyo y cariño que me han demostrado siempre. Al Dr. Javier Tejero y a la Dra. Montserrat Iborra por toda la ayuda y dedicación que me han brindado. Gracias a ellos me he sentido acompañada durante todo el proceso de realización de este trabajo. Y al Dr. Roger Bringué y al Dr. Jordi Hug Badía por la ayuda proporcionada durante mis primeros días con la instalación.

REPORT

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1. SUMMARY

This project is part of the study of the synthesis of butyl levulinates. Butyl levulinates have a number of properties that make them attractive for inclusion in liquid fuel formulations for both diesel and gasoline. In particular, sec-butyl levulinate is known to improve the anti-knock quality of gasoline.

Furthermore, the proposed synthesis route is the esterification of levulinic acid with an olefin, 1-butene. This route, unlike the more traditional routes that employ an alcohol as an esterifier, is not so limited by the extent of secondary reactions. Levulinic acid is a platform compound, derived from lignocellulose and therefore part of what are known as renewable resources based on inedible biomass. In turn, the use of low value-added olefinic streams, such as C_4 streams containing linear butenes, which are often burned in refineries, would make it possible to revalue a non-renewable resource and reduce the resulting environmental impact.

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Thus, given the current European legislative framework, which on the one hand requires a minimum of 10% vol. of biofuels by 2020 and on the other hand allows products with a partially renewable origin, such as sec-butyl levulinate, to be counted as biofuels, it is of interest in the short and medium term to study the production of this type of compound.

Therefore, in view of the potential industrial implementation of this process, one of the key aspects is the selection of the optimal catalyst, and the other is the determination of the thermodynamics of the reaction. In this sense, the use of ion exchange resins is proposed because they allow high yields to be obtained at relatively low operating temperatures and because they are a type of catalyst that is significantly cheaper than other alternatives in the sector. Of the different commercial options for ion exchange resins available, previous work concluded that Amberlyst 15 appears to be the one that maximizes the production of the desired compound. This catalyst has been used to perform the thermodynamic study of the reaction.

The value of the equilibrium constant has been obtained at four different temperatures (90-120 ºC). Due to the high value of the equilibrium constant, it has been considered that the equilibrium is mainly displaced towards the products. The values of the equilibrium constant of SBL formation at different temperatures show that the reaction is exothermic. The value of the standard reaction enthalpy has been estimated.

Keywords: biofuel, sec-butyl levulinate, equilibrium constant, levulinic acid, ion exchange resin, biomass.

2. RESUMEN

Este proyecto se enmarca en el estudio de la síntesis de levulinatos de butilo. Los levulinatos de butilo presentan un conjunto de propiedades que los hacen atractivos de cara a incluirlos en formulaciones de combustibles líquidos, tanto para diésel como para gasolina. En particular, es sabido que el sec-butil levulinato mejora la calidad antidetonante de la gasolina.

Por otra parte, la ruta de síntesis que se propone es la esterificación de ácido levulínico con una olefina, 1-buteno. Esta ruta, a diferencia de las rutas más tradicionales que emplean un alcohol como agente esterificador, no está tan limitada por la extensión de reacciones secundarias. El ácido levulínico es un compuesto de plataforma, derivado de lignocelulosa y que, por tanto, forma parte de lo que se conoce como recursos renovables basados en biomasa no comestible. Por su parte, el uso de corrientes olefínicas de bajo valor añadido, tales como corrientes C_4 que contienen butenos lineales y que a menudo se queman en las refinerías, permitiría revalorizar un recurso no renovable y reducir el impacto ambiental que se deriva.

Así, dado el actual marco legislativo europeo, que por un lado exige un mínimo de 10% vol. de biocombustibles para 2020 y que, por otra parte, permite contabilizar como biocombustible productos con un origen parcialmente renovable, como es el caso del sec-butil levulinato, hace que el estudio de la producción de este tipo de compuestos se convierta de interés a corto y medio plazo.

De cara, pues, a la potencial implementación industrial de esta síntesis, uno de los aspectos claves es la selección del catalizador óptimo, y el otro es la determinación de la termodinámica de la reacción. En este sentido, se propone el uso de resinas de intercambio iónico porque permiten obtener altos rendimientos a temperaturas de operación relativamente bajas y porque son un tipo de catalizadores sensiblemente más económicos que otras alternativas en el sector. De entre las diferentes opciones comerciales de resinas de intercambio

iónico disponibles, en un trabajo previo se concluía que la Amberlyst 15 parece ser la que maximiza la producción del compuesto deseado. Se ha utilizado este catalizador para realizar el estudio termodinámico de la reacción.

Se ha determinado el valor de la constante de equilibrio a cuatro temperaturas diferentes (90-120 ºC). Debido a que el valor de la constante de equilibrio es elevado, se ha considerado que el equilibrio está desplazado principalmente hacia los productos. Los valores de la constante de equilibrio de la formación del SBL a diferentes temperaturas muestran que la reacción es exotérmica. Se ha estimado el valor de la entalpía estándar de la reacción.

Palabras clave: biocombustible, sec-butil levulinato, constante de equilibrio, ácido levulínico, resina de intercambio iónico, biomasa.

3. INTRODUCTION

3.1. FOSSIL FUELS

Fossil fuels are hydrocarbons formed from organic waste from millions of years ago that have been transformed by the pressure and temperature exerted by the sediments accumulated above them. They are considered non-renewable energy sources and three main types are distinguished: in the form of gas, natural gas, in liquid form, crude oil and derivatives, and in solid form, coal.[1] All fossil fuels can be burned to provide heat. This reaction is between the fuel and the oxidant, usually oxygen, which produces water and carbon dioxide.[2]

Although they had been known for a long time, it was not until the XVIII century that they began to be exploited as an energy source. Before, the energy demand was satisfied by the combustion of wood, but, with the arrival of the industrial revolution, it increased causing the need to look for new sources of energy. New technologies made mass production possible by causing high energy consumption and a change in the pace of people's lives. Therefore, with the arrival of the steam engine, coal began to be marketed on a large scale due to the energy factor and because it was easier to transport.[3]

Over time, new technologies led to the commercialization of oil and, with it, the study of its potential uses.[3] It was discovered that by refining crude oil it was possible to obtain intermediate materials and fuel products with use in different areas.[4]

Today, fossil fuels account for approximately 80 percent of the global energy supply,[5] which has led to significant costs both economically and environmentally. From an economic point of view, limited resources and growing demand results in rising prices, and from an ecological point of view, burning large amounts of fuel releases a large amount of greenhouse gases that contributes to climate change.[2]

In recent years, the search for alternative fuels has accelerated due to the depletion and environmental problems of fossil fuels.[4] That implies a coordinated political effort at both government and private sector level.[5] This is why the European Union is part of the global climate agreement, created at the Paris conference in 2015. The agreement establishes a global action plan to keep the increase in global temperature below 2 ºC and continue efforts to keep it at 1.5 ºC. To achieve a progressive reduction in greenhouse gas emissions, a number of key objectives have been set over the years. For 2020, a 20% reduction in greenhouse gas emissions compared to 1990 levels, 20% energy consumption from renewable energy sources and a 20% increase in energy efficiency have been set.[6]

3.2. BIOMASS AND BIOFUELS

Biomass is a source of carbon from animal or plant organic matter that can be used as a raw material for energy and chemicals production. It is a renewable energy source since the emission of carbon dioxide generated during the combustion of biofuels is equivalent to that consumed by plants during photosynthesis, which doesn't increase the amount of greenhouse gases present in the atmosphere.[7]

To be able to produce energy from biomass, it is necessary to carry out a conversion process by means of combustion, gasification, pyrolysis, anaerobic digestion or fermentation. Combustion consists of burning flammable material in the presence of air or oxygen to release heat. This process is the simplest of all and is normally used to heat spaces or to heat steam for power generation. Gasification is carried out through a partial combustion of biomass to produce a mixture of combustible gases called Producer Gas (CO_2 + CO + H_2 + CH_4) or Syngas (CO + H_2). The pyrolysis process takes place through the anaerobic thermal decomposition of biomass from which, depending on the established parameters, different proportions of bio-oil, biochar and synthesis gas are obtained. Anaerobic digestion, also known as bio-digestion, is based on the use of anaerobic bacteria to decompose biomass into biogas and solid waste that can be burned to produce energy. Fermentation is the conversion of glucose or carbohydrates into alcohol or acid by yeasts or bacteria that break down sugars. Therefore, one process or another is carried out to obtain a certain product.[8][9]

Biofuel is a group of organic substances derived from biomass and whose function is to produce energy through combustion.[7] Biofuels come from biorefineries, which are facilities that integrate biomass conversion processes and equipment to produce transport biofuels, energy, and chemicals. Depending on the origin of the feedstock, four types of biofuels can be distinguished.

The first generation of biofuels comes from food crops such as corn and wheat. This resource is unsustainable in the long term because it competes with both human and animal food, resulting in a significant increase in crop prices.

The second generation of biofuels consists of inedible materials from feedstocks derived from lignocellulosic biomass and crops residues from agriculture and forestry. This type of material can be cultivated on a large scale for the sole purpose of producing energy. Due to the nature of cellulosic biomass, fuel synthesis involves pre-treatment to break down the lignin strands. This implies a higher production cost compared to the first generation. To optimize the process, energy crops are required to meet the following properties: a fast growth rate, high tolerance to various environmental stresses, high energy content and relative ease of cultivation compared to food crops.

The third generation of biofuels consists of derivatives of aquatic biomass such as algae. The consideration of microalgae as an alternative energy source is due to their photosynthetic system and high lipid content. Although the technologies in the sector are not fully developed at present, it is estimated that in the future algae will produce much more fuel than crops.[10] This system has a number of disadvantages such as the production of methane that is mixes with water sources. This system has a number of disadvantages such as the emission of methane, which is a greenhouse gas.[6][11]

The fourth generation of biofuels comes from the use of genetically modified algae to improve biofuel production. In recent years, extensive research has been conducted on genetic modification aimed at increasing the productivity of algae strains. However, its application is currently not possible due to legislative limitations on the exploitation and processing of transgenic algae. Therefore, studies are underway on legislation and possible mitigation strategies to address the risks associated with the use of these algae.[12]

There are three general classes of biomass-derived raw materials suitable for the production of renewable fuels: starchy, triglyceride, and lignocellulosic raw materials. We will focus on lignocellulosic biomass because it is the most abundant. This feedstock is composed of lignin (15-20%), hemicellulose (25-35%) and cellulose (40-50%). Lignin is an aromatic polymer based on phenyl-propane units that provide structural rigidity to plants. Hemicellulose is a polysaccharide composed of more than one type of sugar monomer and cellulose is a polymer composed exclusively of β-glucose molecules.[9]

As indicated above, lignocellulosic biomass must be pre-treated in order to be transformed into biofuel. The techniques to transforming this biomass into sugars are as follows: gasification, pyrolysis and hydrolysis. Hydrolysis is the most complex process and requires lignocellulose to be broken into its constituent parts in order to transform cellulose and hemicellulose into C_5 and C_6 sugar monomers.[13]

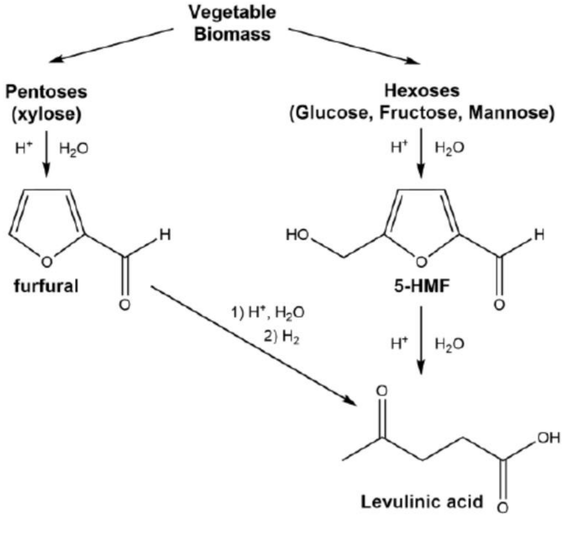


Figure 1. Products obtained by dehydration of monosaccharides.[14]

Chemical transformations of monosaccharides are carried out by thermal dehydration in acidic media, from which the following platform chemicals are obtained: furfural, 5-hydroxymethyl-furfural (HMF), and levulinic acid (Figure 1).[14] Platform chemicals are intermediate molecules with a flexible chemical structure capable of generating a wide range of potential derivatives at a competitive cost.[15]

3.3. LEVULINIC ACID

Levulinic acid (LA), also known as 4-oxopentanoic acid, is a short-chain fatty acid derived from the chemical transformation of sugars from lignocellulose. It is known as an ideal chemical platform due to the capacity to form a wide range of derivatives because of the reactivity of the different functional groups that constitute the molecule of the levulinic acid. Consequently, it has been highlighted as a promising component for chemical industry by the United States Department of Energy in 2004 and 2010.[13]

Chemicals obtained from LA are currently used in various applications, such as solvents, resins, chemical intermediates, polymers, adsorbents, plasticizers, cosmetics, textiles and pharmaceuticals. In addition, LA derivatives can also be used as gasoline and biodiesel enhancers due to their low toxicity and good physicochemical properties.[16]

The Biofine process of 1996 is one of the most famous technologies for obtaining LA using lignocellulosic biomass. It consists of an acid hydrolysis at high temperature composed of two catalytic stages in which high yields of levulinic acid and formic acid (FA) are obtained from hexose polymers.[17] Firstly, in a plug flow reactor, the biomass is mixed with sulfuric acid (1.5 - 3% in weight) where the carbohydrates are hydrolyzed in hydroxymethyl-furfural (HMF) using a mineral acid catalyst at a temperature of 483 - 493 K and pressure of 25 bars with a short residence time, to avoid the formation of secondary products. Then, in a CSTR, the HMF is converted into LA and FA at 463-473 K and 14 bars with a residence time of approximately 20 minutes. The conditions of this process have been optimized to obtain final levulinic acid yields of 70 - 80% of the theoretical maximum, corresponding to 50% of C_6 sugars mass.[9]

3.4. ALKYL LEVULINATES

Alkyl levulinates are biologically based chemical compounds with the potential from use in a variety of applications,[13] one of the most prominent being their use as cold flow improvers in biodiesel and as oxygenated additives for gasoline and diesel fuels. This is because they have low toxicity, high lubricity, flash point stability, and moderate flow properties in low temperature conditions.[18]

Levulinate esters can be obtained by esterification of levulinic acid with alcohols by homogeneous or heterogeneous acid catalysis. The first studies were mainly performed with homogeneous catalysis through direct reaction between LA and alcohol in the presence of hydrochloric acid. Nowadays, the use of heterogeneous catalysts is studied because they increase the levulinate yield, facilitate the separation of the reaction mixture and can be recycled, regenerated or reused. These catalysts are usually acidic, generally solid Brønsted acids, as their use limits the corrosion and elimination problems present in the use of liquid mineral acids. The mechanisms proposed for the esterification of LA on acidic surfaces involve adsorption through the protonated carbonyl group of carboxylic function, which allows the nucleophilic attack of the alcohol assisted by an oxygen atom from the oxide network.[19]

To guaranty the quality of European diesel fuels, they must comply with the specifications indicated in the EN 590 standard, present in Directive 2009/30 /EC (Table 1). These specifications are not mandatory, but guarantee the basic properties for a fuel to be acceptable. Therefore, fuel suppliers in Europe follow them.[14]

The cetane number is a parameter associated with the resistance to self-ignition of diesel fuels. The ignition delay is the time interval between the start of fuel injection and the moment it starts to burn. Fuels with a high cetane number have a very short ignition delay time. This parameter is influenced by various physicochemical phenomena associated with the nature of the fuel. For diesel cycle engines, a high cetane number is of interest to avoid excessive fuel consumption, increased power loss and possible engine damage.[20]

Fuel property	Unit	Specification		Test
		Min	Max	
Cetane Number	-	51	-	ISO 5165
Cetane Index	-	46	-	ISO 4264
Density (15ºC)	kg/m^3	820	860	ISO 365 / ASTM D4052
Sulfur	ppm	-	50	EN 24260 / ISO 8754
Flash Point	ºC	55	-	ISO 2719
Carbon residue (10% btms)	% (wt.)	-	0.30[a]	ISO 10370
Ash	% (wt.)	-	0.01	EN 26245
Water content	mg/kg	-	200	ASTM D1744
Copper strip corrosion, 3h (50ºC)	-	-	Class 1	ISO 2160
Oxidation stability	g/m^3	-	25	ASTM D2247
Viscosity (40ºC)	mm^2/s	2.00	4.50	ISO 3104
Distillation (vol. % recovered)	ºC			ISO 3405
10% point	ºC	report	-	
50% point	ºC	report	-	
65% point	ºC	250	-	
85% point	ºC	-	350	
95% point	ºC	-	370	
FAME content	% (wt.)	7	-	

(a) limit does not apply if ignition improver additives are used.

Table 1. Directive 2009/30/EC Diesel fuel specification. [14]

The cetane number is a parameter associated with the resistance to self-ignition of diesel fuels. The ignition delay is the time interval between the start of fuel injection and the moment it starts to burn. Fuels with a high cetane number have a very short ignition delay time. This parameter is influenced by various physicochemical phenomena associated with the nature of the fuel. For diesel cycle engines, a high cetane number is of interest to avoid excessive fuel consumption, increased power loss and possible engine damage.[20]

Density and viscosity are parameters related to the combustion process that influence fuel atomization.[21] A minimum density value ensures sufficient power to the engine, while an excess can lead to smoke production.[14] Viscosity is a measure of flow resistance. Too viscous fuel can damage the fuel pump due to increased pressure. However, too low a viscosity would lead to a lack of lubrication.[22]

The sulfur content should be as low as possible due to the corrosive effects on various engine components and the generation of sulfur oxides during combustion. This produces a decrease in the lubrication of the fuel which can be remedied by adding additives that compensate for this.[23][24]

The volatility characteristics are specific because they must be suitable for the injection process and must facilitate the spraying of the fuel. Generally, volatility is defined by the distillation curve as it provides a range of temperatures over which the fuel is vaporised.[25]

When a diesel fuel cools down, the cloud point can be reached. This is the temperature at which the paraffin crystallizes into wax causing the fuel to become cloudy. It is also possible to reach the pour point that corresponds to the temperature from which the fuel stops flowing. The flash point is defined as the minimum temperature at which diesel fuel must be heated to release sufficient vapors that, in the presence of air, ignites on contact with a flame.

Water content in diesel fuels should be kept to a minimum as they cause corrosion of fuel lines, pumps and injection components. Therefore, automotive fuels are intended to have low water miscibility. The carbon residue is used as an indicator to measure the amount of carbon deposits left after the fuel is burned.[23]

The most studied alkyl levulinates as fuel additives are ethyl levulinate (EL) and butyl levulinate (BL). Although most studies have focused on the synthesis of EL, BL has been found to be more promising as a fuel additive.[26] Below is a table with the properties of both esters as additives to diesel fuel.

PROPERTIES	**Ethyl levulinate (EL)**	**Butyl levulinate (BL)**
Freezing point	< – 60 ºC	< – 60 ºC.
Boiling point	206 ºC	237.5 ºC
Flash point	90 ºC	110 ºC
Lubricity	430 μm	310 μm
Conductivity	Increase	Increase
Kinematic viscosity	1.5 cSt	1.99 cSt
Particulate emission	Decrease	Decrease
Cetane number	5	14
Solubility of ester in water	15.2% w/w	1.3% w/w
Solubility of water in ester	8.5% w/w	2.6% w/w
Density at 15 ºC	1010 kg/m^3	970 kg/m^3
Lower heating value	24.8 MJ/L	27.1 MJ/L
Diesel fuel at 20% levulinate	Immiscible at T < – 10 ºC	Immiscible at T < – 25.8 ºC

Table 2. Properties of esters as additives to diesel fuel.[17]

In addition to the use of EL and BL, there is another alternative fuel additive not previously studied, sec-butyl levulinate (SBL). This comes from the esterification of LA by olefins instead of alcohols, thus avoiding the lateral formation of dialkylether and water as by-products.[27] The use of this reaction would solve the problem that occurs in petrochemicals with 1-butenes, since they have no other outlet than the manufacture of polybutene.[28] This means that in the low season they are burned to prevent their accumulation. Therefore, the incorporation of this study to the industry would produce a revaluation of these olefins. Another advantage of their use is the reformulation of the biofuel using compounds derived from biomass.

3.5. ACID ION EXCHANGE RESINS

A catalyst is a substance that increases the rate at which a chemical reaction approaches equilibrium without permanently intervening in the reaction. Depending on the nature of the catalyst, catalysis can be classified into three different types. Homogeneous catalysis, where the catalyst is in the same phase as the reactants, heterogeneous catalysis, where reagents and catalyst are in different phases, and enzymatic catalysis, where the catalyst is an enzyme. Approximately 80% of industrial catalytic processes are of the heterogeneous type and 90% of these use solid catalysts.

For a solid to act as a catalyst, it is necessary for at least one of the reagents to interact with the surface of the solid and be adsorbed onto it. Since it is essential to have a large surface area where the reagents can be adsorbed, porous solids are usually used. The structure of the solid particles of catalyst, the number, size and volume of the pores being more exact, is fundamental for the performance of the catalyst. The chemical composition of the catalyst must also be taken into account since the interaction of the reagent with the surface is chemical in nature. The steps of a solid catalytic reaction take place in the active centers of the solid and correspond to the adsorption of reactants, the surface reaction and the desorption of the product. The industrial interest of a given solid catalyst is evaluated in terms of selectivity, useful life and activity.[29]

Ion exchange resins are organic polymers capable of exchanging ions with the medium in which they are immersed and their structure consists of a polymeric matrix with anchored functional groups. The cross-linking agent gives the matrix a stable three-dimensional hydrophilic structure with a defined pore structure.[14]

Among a wide variety of ion exchange resins, the most widely used are those with styrene-divinylbenzene (PS-DVB) matrixes. These resins are obtained by polymerization of styrene and the addition of a specific amount of divinylbenzene (DVB). Depending on the polymerization process there are two main types of resins: gel type (microporous) and macroreticular (macroporous). Gel-type resins are obtained by means of a suspension of styrene and DVB in water that provides a homogeneous structure without discontinuities. However, macroreticular resins are manufactured by adding an organic solvent to the styrene and DVB suspension. This solvent does not react with the compounds in the suspension and when extracted creates permanent spaces that break up the gel-like structure.[30] Subsequently, a sulfonation process is carried out, which consists of a bath with concentrated sulfuric acid, so that it acquires the desired acid properties. Depending on the degree of sulfonation, the following three groups are distinguished: over-sulfonation (OS), conventional sulfonation (CS) and surface sulfonation (SS) in descending order from the highest to the lowest sulfonation.[31]

The porosity of a resin is related to the degree of cross-linking and there are two main types of resins: gel type and macroreticular. Low cross-linking resins usually have a microporous structure, while higher grades of cross-linking usually result in macroporous resins. Porosity affects some bulk properties of the resins that have consequences on their catalytic applications, that is, swelling, capacity, equilibrium rate and selectivity.[32] Depending on the pore diameter provided by the matrix, the resins have different types: ultramicropores (< 0.7 nm), micropores (< 2 nm), mesopores (between 2 nm and 50 nm) and macropores (> 50nm).[33]

The specific properties of the resins are defined both by the functional groups and the polymer matrix and by the structure of the polymer, which depends on the polymerization method implemented. The use of this type of catalysts has a series of advantages such as the reduction of corrosion of the equipment, the ease of product separation, less potential contamination in the waste streams and the recycling of the resin. All these advantages favor cost reduction.[14][34]

The parameters that determine the use of a certain resin are: degree of cross-linking, swelling, stability, particle diameter, density, affinity to water and acid capacity.

The degree of cross-linking corresponds to the weight percentage ratio of the cross-linking agent (DVB) present in the initial monomer solution before the polymerization process. Cross-linking provides stiffness to the matrix and reduces the number of larger pores. A resin with a high degree of cross-linking swells moderately in aqueous solution and therefore has a lower volume loss during drying. However, it causes internal mass transfer problems that affect the reaction rate.[35]

Swelling capacity is the variation in volume of a resin when it interacts with the polar medium due to the difference in osmotic pressure between the inside and outside.[31] Knowledge of this parameter is crucial to determine the behavior of the resin in the presence of a solvent.[32]

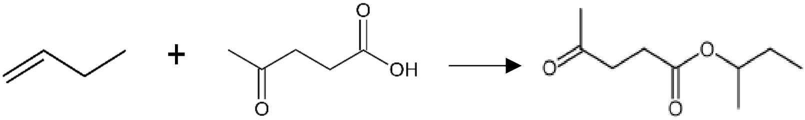
Density is the ratio of the dry mass of the resin per unit volume and is determined by the matrix structure, the functional groups, and the degree of cross-linking. The water content is defined as the ratio of water in the mixture to total mass of hydrated resin. The acid capacity corresponds to the number of accessible sulfuric groups in the swollen resin and is determined by acid-base titration.[31]

Since ion exchange resins must operate for long periods of time, they must be chemically, mechanically and thermally stable. Chemical stability is the ability of a resin to work under oxidizing conditions without undergoing changes in the polymer structure. Resins with a high cross-linking percentage are more resistant against an oxidizing medium than resins with a low percentage. The mechanical stability corresponds to the tolerance of the resin against compression and breakage. Macroreticular resins are more rigid than gel-type resins because they have a more cross-linked structure. Thermal stability is defined as the ability of the resin to withstand high temperatures. This capacity is related to the degree of cross-linking. Therefore, macroreticular resins have lower thermal stability than gel-type resins.[31]

The knowledge of the above parameters is useful to understand the catalytic behavior of a resin in the reaction environment.[33] Démolis et al. studied the reactivity of LA with 1B in the presence of H_2SO_4 with a catalyst. In order to eliminate the need to separate the liquid catalyst from the product, the esterification of LA in the presence of an acidic ion exchange resin as a solid catalyst was studied. The resin that obtained the best results was Amberlyst 15 (A15).[27] The basic information of this resin can be found further in Table 11.

3.6. EQUILIBRIUM CONSTANT

The objective of this study is to obtain the equilibrium constant of esterification of LA with 1-butene using an ion exchange resin as a catalyst.



Scheme 1. Esterification of Levulinic Acid with 1-Butene.

The equilibrium constant will be determined both experimentally and theoretically. For the theoretical calculation, the necessary parameters will be obtained of the literature or by means of estimates. Experimentally, the reaction shall be carried out under different temperature conditions. Once the reaction reaches equilibrium, the constant will be calculated through the equilibrium concentrations of the species and compared to the theoretical one.

3.6.1. Definition of enthalpy

Gibbs discovered that, when energy is added to matter, the randomness of the matter varies at the molecular level or is added to or removed from the substance. Changes corresponding to the substance's disorder were defined as entropy and heat-related changes as enthalpy.[36]

In chemical reactions, reaction enthalpy is defined as the variation of enthalpy produced by the reaction under constant conditions of temperature and pressure per unit mass or mole of the product formed or reagent consumed. If the variation is negative, it means that heat is given off and the reaction is exothermic, while if it is positive, heat is absorbed and the reaction is endothermic. To facilitate the tabulation of the enthalpy values, a standard state of pressure and temperature equivalent to 1 atm and 25 ºC was defined.

The standard enthalpy of formation is defined as the heat required to produce one mole of a substance in the standard state. If the formation values for all the reaction compounds are known, the standard enthalpy of the reaction can be calculated using the following equation:[37]

$$\Delta H_r^o(298K) = \sum_{i=j} v_j \cdot \Delta H_{f,j}^o \tag{1}$$

3.6.2. Definition of entropy

The second law of thermodynamics allows the characterization of a state function called entropy. The variation of entropy of a system is a reference to interpret the evolution of an isolated system. When the system is not isolated, it is used to determine whether the reaction is reversible or irreversible.[37]

$$dS \geq \frac{\delta q}{T} \tag{2}$$

If the process is adiabatic:

$$dS \geq 0 \tag{3}$$

Where if dS = 0 the process is reversible and if dS > 0 the process is irreversible.

The standard entropy of the reaction can be obtained using the values of standard entropy of compounds present in the chemical reaction:[37]

$$\Delta S_r^o(298K) = \sum_{i=j} v_j \cdot S_j^o \tag{4}$$

3.6.3. Definition of equilibrium

Chemical equilibrium is a state of the reaction system where the rate of the forward reaction is equal to the rate of the reverse reaction.[38] The speed at which a reversible reaction reaches equilibrium depends on the temperature and the concentration of reactants and products present in the system. In case the reaction is slow, a catalyst is usually used in the industry to accelerate the reaction.[29]

If we consider a reversible reaction of one mole of A with one mole of B producing one mole of C under constant pressure and temperature conditions:

1. $\upsilon_A A + \upsilon_A B \rightleftharpoons \upsilon_C C$

Where 2 is the forward reaction and 3 the reverse reaction:

2. $\upsilon_A A + \upsilon_A B \rightarrow \upsilon_C C$
3. $\upsilon_C C \rightarrow \upsilon_A A + \upsilon_A B$

The law of mass action determines that the reaction rate is directly proportional to the product of the concentration of the reactants raised to their stoichiometric coefficients. Therefore, the forward and reverse reaction rates are determined as follows:

$$r_2 = k_{forward}[C]^{\upsilon_C} \tag{5}$$

$$r_3 = k_{reverse}[A]^{\upsilon_A}[B]^{\upsilon_B} \tag{6}$$

Where k is rate constant of the forward or reverse reaction.

The equilibrium constant is the parameter that characterizes the chemical equilibrium and is defined as the quotient between the rate constants of the forward and reverse reaction. The equilibrium constant is a function of temperature only.

$$K = \frac{k_{forward}}{k_{reverse}} = \frac{[C]^{\upsilon_C}}{[A]^{\upsilon_A}[B]^{\upsilon_B}} \qquad (7)$$

3.6.3.1.Thermodynamic equilibrium constant

Considering the above reversible reaction, the state of chemical equilibrium is reached when:

$$\sum_i \upsilon_i \mu_i = 0 \qquad (8)$$

Where μ is the chemical potential of species i. If the products and reagents are miscible liquids, the chemical potential of species i at the chemical equilibrium is:

$$\mu_{i,eq} = \mu_i^0 + RT \ln a_{i,eq} \qquad (9)$$

Where μ_i^0 is the standard chemical potential and a_i is the activity of species i.

Substituting equation 9 in the chemical equilibrium condition (Eq. 8) we obtain:

$$\sum_i \upsilon_i \mu_i^0 + RT \ln \prod_i \upsilon_i a_i = 0 \qquad (10)$$

The thermodynamic equilibrium constant of the reaction is defined as the product of the activities of the species in equilibrium raised to the respective stoichiometric coefficients. It is a positive and dimensionless magnitude that is usually represented by K_a.

$$K_a = \prod_i {a_{i,eq}}^{\upsilon_i} = \frac{{a_C}^{\upsilon_C}}{{a_A}^{\upsilon_A}{a_B}^{\upsilon_B}} \qquad (11)$$

The Gibbs energy variation is:

$$\Delta G^0 = -RT \ln \prod_i {a_{i,eq}}^{v_i} = -RT \ln K_a = \Delta H^0 - T \cdot \Delta S^0 \tag{12}$$

3.6.3.2. *Kirchhoff's equation*

The Kirchhoff equation allows to calculate enthalpy reaction changes at different temperatures. It is a very important equation in thermodynamics since the enthalpy change is usually not constant over large temperature intervals.

$$\Delta H_r(T_2) = \Delta H_r(T_1) + \int_{T_1}^{T_2} \Delta C_p dT \tag{13}$$

Adapting the above equation to this case:

$$\Delta H_r^o(T) = \Delta H_r^o(298K) + \int_{298K}^{T} \sum_i v_i \cdot C_{pL,i}(T)\, dT \tag{14}$$

For the variation of entropy at temperatures other than 25°C, the following expression applies:

$$\Delta S_r^o(T) = \Delta S_r^o(298K) + \int_{298K}^{T} \frac{\sum_i v_i \cdot C_{pL,i}(T)}{T} dT \tag{15}$$

4. OBJECTIVES

This work focuses on the study of the liquid-phase synthesis of sec-butyl levulinate by the esterification of levulinic acid with 1-butene, using sulfonated polystyrene-divinylbenzene ion exchange resin as a catalyst. The main objective of this work is the study of the thermodynamic behavior of the reaction. To do so, it is necessary:

1. Determine the thermodynamic equilibrium constant experimentally at different temperatures.
2. Estimate the theoretical equilibrium constant and compare it with the experimental values.
3. Determine the thermodynamic parameters of the reaction.

5. ESTIMATION OF THE THEORETICAL CONSTANT

The objective of this study is to determine the values of the chemical equilibrium constant of the esterification of LA with 1-butene as a function of temperature. The chemical equilibrium is characterized by the thermodynamic equilibrium constant (K_a). This constant depends only on temperature. Firstly, we'll proceed to estimate theoretically the equilibrium constant in order to compare it with the values obtained experimentally at different temperatures.

According to the definition of Gibbs energy variation (equation 12), the equilibrium constant can be related to the thermodynamic variables of the reaction. By rewriting eq. 12, a linear relationship between K_a and the reverse of the temperature can be obtained:

$$\ln(K_a) = -\frac{\Delta G^o_{r,l}(T)}{RT} = -\frac{\Delta H^o_{r,l}(T)}{RT} + \frac{\Delta S^o_{r,l}(T)}{R} \qquad (16)$$

The standard values of enthalpy and entropy of the reaction are used to estimate the constant. These depend on the formation enthalpies and standard entropies of the compounds present by means of the expressions 1 and 4. In the case where the working temperature is different from the standard (of 25 ºC), the corresponding thermodynamic values are calculated through equations 14 and 15.

These expressions depend on the heat capacity (Cp) of each compound and are a function of temperature. The only value of Cp at 298K found in the literature was that of 1-butene. The others have had to be estimated by the "Ruzicka and Domalski method".[39]

$$C_{pL} = R\left[A + B\frac{T}{100} + D\left(\frac{T}{100}\right)^2\right] \qquad (17)$$

Where R is the gas constant in J/(mol·K) and T is the temperature in kelvins degrees. Parameters A, B and C are determined by the following expressions:

$$A = \sum_{i=1}^{k} n_i a_i \qquad B = \sum_{i=1}^{k} n_i b_i \qquad D = \sum_{i=1}^{k} n_i d_i \tag{18}$$

In order to use this method, it is necessary to separate the compounds into their constituent groups. These groups are related to the parameters of a, b and c whose values are tabulated. n_i is the number of groups of type i and k corresponds to the total number of groups that form the molecule. Table A in Appendix 2 shows the contribution groups for LA, 1B, SBL, trans-2-butene and cis-2-butene used to calculate the functions that relate the Cp of each compound to temperature in kelvins (Table 3).

Compound	$C_{pL,i}$**(T)** [J/mol K]
LA	$C_{pL}(T) = 8.3145 \cdot \left[57.08 - 6.45 \cdot \frac{T}{100} - 0.04 \cdot \left(\frac{T}{100}\right)^2\right]$
1B	$C_{pL}(T) = 8.3145 \cdot \left[14.89 - 1.94 \cdot \frac{T}{100} + 0.62 \cdot \left(\frac{T}{100}\right)^2\right]$
SBL	$C_{pL}(T) = 8.3145 \cdot \left[60{,}63 + 1.78 \cdot \frac{T}{100} - 1.81 \cdot \left(\frac{T}{100}\right)^2\right]$
trans-2B/cis 2B	$C_{pL}(T) = 8.3145 \cdot \left[15.84 - 2.83 \cdot \frac{T}{100} + 0.82 \cdot \left(\frac{T}{100}\right)^2\right]$

Table 3. Estimated Cp values.

The estimated value of Cp for 1B at standard temperature is compared with that found in the literature. At 25 ºC, the equation predicts a value of 121.2 J/mol·K which resembles that found in the literature, of 118 J/mol·K.[40]

The standard values of formation enthalpy and entropy are tabulated for most compounds, as 1-butene, levulinic acid and 2-butene trans and cis. But for compounds whose thermodynamic values are not known, as sec-butyl levulinate, such properties have to be determined.

5.1. STANDARD ENTHALPY OF THE SBL FORMATION

For the estimation of the standard enthalpy of formation of the SBL in the liquid state, the formation enthalpy for the gas state and the condensation enthalpy are required.

The "Joback method" is used to calculate the standard formation enthalpy in the gas state. This is based on the energy corresponding to each group that makes up the molecule.[39] The expression to be used is as follows:

$$\Delta H_f^o(298.15K) = 68.29 + \sum_k N_k \cdot \Delta hfk \tag{19}$$

Where N_k is the number of k-type groups present in the molecule and Δhfk is the characteristic value of the group k. The tabulated values used from Δhfk for the SBL are given in Table B of Appendix 2.

To change from gas to liquid formation enthalpy, it is necessary to estimate the condensation enthalpy of the product. This requires the determination of both the boiling temperature and the critical temperature and pressure. The "Joback method" should be applied because the groups forming the molecular structure are used to determine these parameters.[39]

The boiling temperature (T_b) is estimated by the following expression:[39]

$$T_b[K] = 198 + \sum_k N_k \cdot (tbk) \tag{20}$$

The critical temperature (T_c) and critical pressure (P_c) are obtained using the following equations:[39]

$$T_c[K] = T_b \cdot \left[0.584 + 0.965 \cdot \left\{\sum_k N_k \cdot (tck)\right\} - \left\{\sum_k N_k \cdot (tck)\right\}^2\right]^{-1} \tag{21}$$

$$P_c[bar] = \left[0.113 + 0.0032 \cdot N_{atoms} - \sum_k N_k \cdot (pck)\right]^{-2} \tag{22}$$

Where N_{atoms} is the number of atoms in the molecule, N_k is the number of k-type groups present and tbk, tck and pck are the tabulated values corresponding to the k-group for boiling temperature, critical temperature and critical pressure, respectively. The values used are in Table C of Appendix 2.

Considering that the number of atoms in the compound is 28, the values for SBL are as follows:

T_b [K]	**T_c** [K]	**P_c** [bar]
517	701	24.85

Table 4. T_b, T_c and P_c values of the SBL.

Condensation enthalpy has the same value as vaporization enthalpy, but with the opposite sign. Therefore, the vaporization enthalpy will be estimated and its sign changed. The method to be used will be the "Vetere method" which uses the boiling temperature and the critical pressure to estimate it.[39]

$$\Delta H_{vb} = R \cdot T_b \cdot \left[\frac{(1 - T_{br})^{0.38} \cdot \left(\ln P_c - 0.513 + \frac{0.5066}{P_c \cdot T_{br}^2} \right)}{1 - T_{br} + F \cdot (1 - (1 - T_{br})^{0,38}) \cdot \ln T_{br}} \right] \tag{23}$$

Where T_{br} is the division between T_b and T_c and F is a parameter equal to 1.

Since the vaporization enthalpy obtained is for the boiling temperature, it has to be converted to the standard temperature (T_o = 298.15 K) by means of Watson's ratio:[39]

$$\Delta H_{cond.,To} = \Delta H_{cond.,Tb} \cdot \left(\frac{1 - T_{or}}{1 - T_{br}} \right)^{0,38} \tag{24}$$

Where T_{or} is the quotient between T_o and T_c.

Once these two enthalpies have been estimated, the standard enthalpy of SBL formation in the liquid state is calculated using the following equation:[39]

$$\Delta H_f^{\circ}(T_o, l) = \Delta H_f^{\circ}(T_o, g) + \Delta H_{cond.}(T_o) \tag{25}$$

The values obtained from these enthalpies are shown in Table 5.

ΔH_f^o (T_o,g) [kJ/mol]	**$\Delta H_{cond.}$ (T_b)** [kJ/mol]	**$\Delta H_{cond.}$ (T_o)** [kJ/mol]	**ΔH_f^o (T_o,l)** [kJ/mol]
-664	-50.20	-67.63	-732

Table 5. Enthalpy values for the SBL.

5.2. STANDARD ENTROPY OF SBL

As the standard molar entropy of the SBL is not found in the literature, the theoretical estimation of the calorific capacities of the product in both states and the condensing enthalpy at boiling temperature has to be made by means of the standard molar entropy in the gas phase:

$$S^o_{SBL}(T_o,l) = S^o_{SBL}(T_o,g) + \int_{T_o}^{T_b} \frac{C^0_p(T)}{T}dT + \frac{\Delta H_{cond.}(T_b)}{T_b} + \int_{T_b}^{T_o} \frac{C_{pL}(T)}{T}dT \quad (26)$$

To obtain the entropic value of the SBL in the gas state, the "Benson method" has been used because it takes into account the molecular symmetry:[39]

$$S^o(298.15K) = \sum_k N_k \cdot (S^o_k) + S^o_s \quad (27)$$

$$S^o_s = R \cdot \ln(N_{oi}) - R \cdot \ln(N_{ts}) \quad (28)$$

$$N_{ts} = N_{es} \cdot \prod_{k=term} (N_{is})_k \quad (29)$$

Where S^o_s corresponds to the symmetry entropy, N_k is the number of k-type groups present, S^o_k is the characteristic value of each group and R is the gas constant (J/mol·K). The symmetry entropy depends on the number of structural isomers of the molecule, N_{oi}, and the total symmetry number, N_{ts}. The N_{ts} is a function of the number of possible external confirmations that are indistinguishable by rotating the molecule as if it were rigid, N_{es}, and the number of possible indistinguishable internal configurations by rotating the terminal groups on their links to the internal groups, N_{is}. The values of S_k used are given in Table D of Appendix 2.

For the calculation of the integral of the heating capacity in gas state it has been necessary to estimate this capacity as a function of temperature. The "Joback method" has been used for this purpose:[39]

$$C_p^o(T) = \left\{\sum_k N_k \cdot (CpAk) - 37.93\right\} + \left\{\sum_k N_k \cdot (CpBk) + 0.210\right\} \cdot T + \left\{\sum_k N_k \cdot (CpCk) - 3.91E-04\right\} \cdot T^2 + \left\{\sum_k N_k \cdot (CpDk) + 2.06E-07\right\} \cdot T^3 \tag{30}$$

Where N_k is the number of k-type groups and CpAk, CpBk, CpCk and CpDk are the tabulated values of the k-type group. Using the values in Table E of Appendix 2, the following function has been obtained:

$$C_p^o(T) = 25.79 + 0.782 \cdot T - 3.56E-04 \cdot T^2 + 2.93E-08 \cdot T^3 \tag{31}$$

Table 6 shows the values obtained:

N_{oi}	N_{es}	N_{is}	N_{ts}	S_s^o [J/mol·K]	S^o (T_o,g) [J/mol·K]	S^o (T_o,l) [J/mol·K]
1	1	27	27	-27.4	463	470.12

Table 6. Entropy values for the SBL.

Once the enthalpy and entropy values of the SBL at standard temperature have been estimated, the thermodynamic values of the reaction can be calculated using equations 1 and 4. The thermodynamic properties used for the different compounds are shown in Table 7 and the values for the reaction are shown in Table 8:

Compound	**$\Delta_f H^o$(l)** [kJ/mol]	**S°(l)** [J/mol·K]
LA[(a)]	-683.8	268.6
1B[(b)]	-20.8	227.0
SBL[(c)]	-731.9	470.1
trans-2B	-33.3[(b)]	205.31[(d)]
cis-2B[(b)]	-29.8	219.9

(a) Values taken from V.N. Emel'yanenko et al.[41]
(b) Values taken from CRC Handbook of Chemistry and Physics.[40]
(c) Values estimated by The properties of gases and liquids.[39]
(d) Values taken from NIST.[42]

Table 7. Thermodynamic properties of chemical compounds at 298 K.

Property	**T_o = 298,15 K**
$\Delta_r H^o_{(l)}$ [kJ/mol]	-27.3
$\Delta_r S^o_{(l)}$ [J/mol·K]	-25.5

Table 8. Relation enthalpy and entropy values.

To estimate the K_a values for different temperatures, it is necessary to use equations 14 and 15 to obtain the enthalpies and entropies corresponding to those temperatures. The results for the temperature study range are shown in Table 9 for both the main reaction (1) and the isomerization of both 1-butene to trans-2-butene (2) and trans-2-butene to cis-2-butene (3).

T [K]	**K_a^1**	**K_a^2**	**K_a^3**
363	369	4.66	0.497
373	284	4.17	0.507
383	220	3.76	0.525
393	172	3.41	0.541

Table 9. Estimated K_a values.

6. EXPERIMENTAL SECTION

6.1. EXPERIMENTAL MATERIALS

The synthesis of sec-butyl levulinate is performed by using levulinic acid (Acros Organics, code: 125140010, 98% purity) and 1-butene (Air Liquide, 99.9% purity). For the calibration process it was necessary to use analytical standards: 2-butanol (PanReac AppliChem, code: 163851.1611, 99% purity) and butyl levulinate (Sigma-Aldrich, code: 101495705, 98% purity). The main properties of the reagents and products used are listed in Table 10.

PROPERTIES	**levulinic acid**[a]	**sec-butyl levulinate**[d]	**1-butene**[d]	**2-butanol**[b]	**butyl levulinate**[c]
Formula	$C_5H_8O_3$	$C_9H_{16}O_2$	C_4H_8	$C_4H_{10}O$	$C_9H_{16}O_3$
CAS number	123-76-2	85734-01-6	106-98-9	78-92-2	2052-15-5
Molecular weight (g/mol)	116.12	172.22	56.11	74.12	172.22
Density (kg/cm3)	1.134	-	0.608	0.807	0.974
Boiling point (ºC)	245.5[d]	-	-6.11	99.5	237.5[d]
Flash point (ºC) at 1 atm	98	-	-78.9	24[d]	92
Melting point (ºC)	33[d]	-	-185.3	-114.3	-

(a) Value obtained from Acros Organics.
(b) Value obtained from PanReac AppliChem.
(c) Value obtained from Sigma-Aldrich.
(d) Value obtained from PubChem.

Table 10. Main properties of the reactants and products.

The ion exchange resin used as a catalyst is Amberlyst 15 (A15) which has the following properties:

Catalyst	Type	Sulfonation	Acid capacity [mmol H^+/g]	DVB% [%]	Water retention [%]	T_{max} [ºC]	ρ [g/cm^3]
A15	macro	CS[a]	4.81	20	52-57	42	1.416

(a) Conventionally sulfonated (CS).

Table 11. Physical and morphological properties of A15 resin.[31]

The gas used for the pressurization of the system was nitrogen (99.9995% purity) and the chromatographic carrier gas was helium (99.9998% purity).

6.2. EXPERIMENTAL SET-UP

The system is made up of a stainless-steel batch reactor with a total volume of 250 mL and a useful volume of 200 mL (Autoclave Engineers, Inc. Serial Nº. E89-10735-1) with an operating overpressure of 25 atm. The system features a thermostatic bath composed of a mixture of 1,2-propanediol and water to control the temperature of the reactor. The reactor contains a stirrer, a relief valve, a pressure gauge, a thermocouple and a baffle plate.

The agitation system consists of a turbine with six blades mounted on a rotor connected to a frequency converter that regulates the agitation speed. Next to the turbine, there is a stainless-steel baffle plate whose function is to break up the vortices created by the agitation. The reaction temperature is measured by a thermocouple (accuracy +/- 1ºC).

The pressure is measured by a manometer located between the relief valve and the reactor. The relief valve is used to depressurize the system in the event of an uncontrolled increase in pressure or to open the reactor.

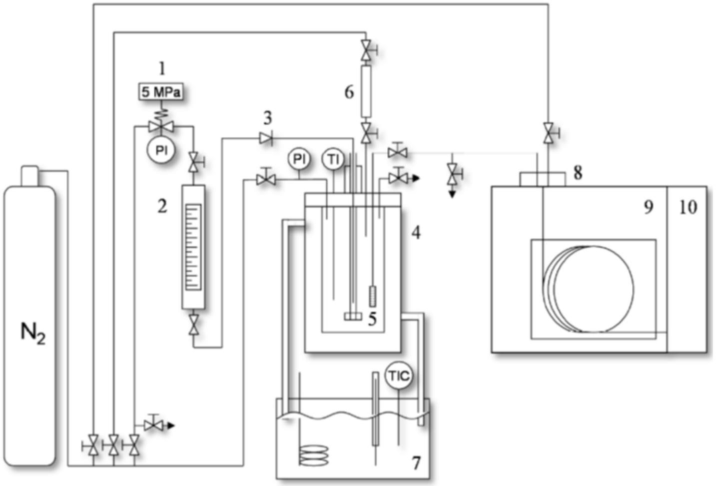


Figure 2. Schematic diagram of the batch reactor setup. 1: safety valve, 2: pressure burette, 3: one-way valve, 4: batch reactor, 5: 05 µm filter, 6: catalyst injector, 7: thermostatic bath,8: sampling valve, 9: gas chromatograph, 10: mass selective detector.[43]

The reactor is connected to a gas chromatograph (Agilent 7890B GC System) coupled to a mass-selective detector (Agilent 5977B GC/MSD) through which analyses are performed. The chromatograph is made up of a capillary column (HP-PONA 19091s-001, J&M Scientific, Santa Clara, US; 100% dimethylpolysiloxane, 50m x 200 µm x 0.5 µm).

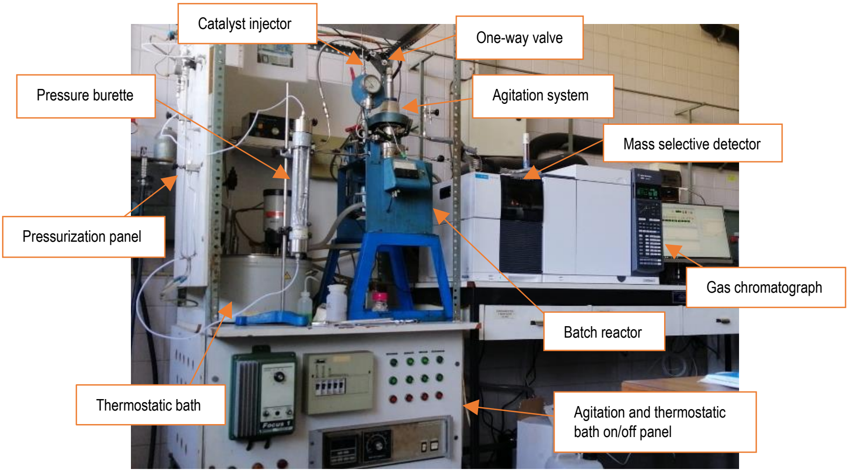


Figure 3. Experimental team.

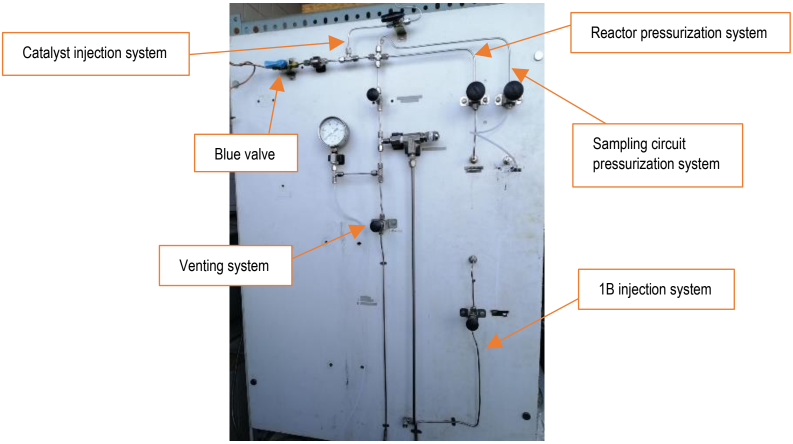


Figure 4. Pressurization panel.

The closed circuit connecting the reactor to the chromatograph is kept at a constant temperature by an electric heating blanket that prevents the sample from solidification during the analysis. Sampling is done through a synthesized iron filter with a 0.5 µm mesh located in the reactor that prevents the passage of the catalyst. The sample aliquots (0.2 µL) are brought to the GC by depression and the injection is done automatically by a mechanically operated valve that uses synthetic air. The method of analysis performed by the chromatograph is described in Appendix 1.

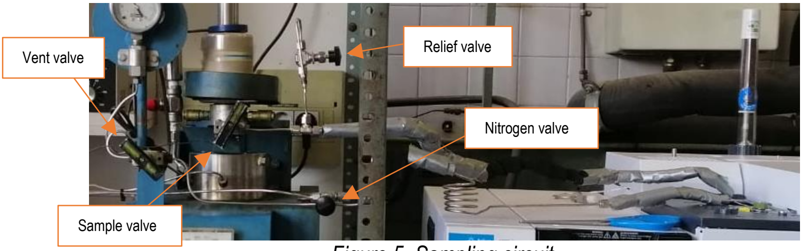


Figure 5. Sampling circuit.

6.3. EXPERIMENTAL PROCEDURE

6.3.1. Catalyst pre-treatment

Ion exchange resins are very hygroscopic and must be pre-treated to remove the water they contain as this causes a decrease in their catalytic activity. The typical procedure to follow is as below:

1. Wash the resins with deionized water several times until the water comes out clean.
2. Let the catalyst dry for 1 or 2 days at room temperature.
3. Weigh the desired amount plus a margin of 5 g of catalyst in a crucible.
4. Allow the resin to dry overnight in an atmospheric oven at 110 ºC (about 12 hours).
5. Then place the container in the vacuum oven at 100 ºC.
6. Turn the valve on the left side of the oven until the blue arrow points downwards and switch on the vacuum pump.
7. Place the oven in the "VACUUM" mode and press the "SET" button (repeat this step several times if it is not activated).
8. Once the vacuum has been reached (10 mbars), switch off the pump and turn the valve until the arrow points up.
9. Leave the crucible in the oven for one hour (while preparing the experiment).
10. To break the vacuum, select the “OPEN DOOR” mode and press “SET”.
11. Open the door when the oven pressure is the atmospheric one.

6.3.2. Reactor load

1. Heat the levulinic acid in a water bath at 40 ºC.
2. Add the desired volume of 1B to the burette and weigh on the scale (adjust the amount until the desired weight is obtained).
3. Place the burette into the system.
4. Recalculate the weight of LA needed from the actual weight of 1B to meet the initial molar ratio.

5. Turn on the thermostatic bath once the maximum temperature to be reached has been adjusted and the level of the bath has been checked (set the power to 100% while heating and lower it to 40% once the temperature has stabilized).
6. Weigh the required LA into a beaker and quickly load it into the reactor to prevent it from solidifying.
7. Close the reactor.
8. Mount the agitation system (chain and cover) and place the agitation speed indicator on top.

When fixing the reactor cover, a safety system was placed to prevent the speed indicator from being placed. Therefore, the stirring speed has been left as it was, at 750 rpm.

9. Place the one-way valve that connects the 1B burette to the reactor.
10. Screw the closed sampling circuit to the sample valve.
11. Turn on the agitation system.
12. Break the vacuum from the oven in order to remove the catalyst (steps 11 and 12 catalyst pre-treatment).
13. Weigh out the required grams of catalyst and insert them into the catalyst injector through the valve just above it.
14. Pressurize the injector to prevent the catalyst from getting wet (up to 25 bars).
15. Check that the temperature in the reactor is as desired using the temperature reader.
16. Introduce 1B into the reactor by depression (without exceeding 15 bars).
17. Introduce the catalyst into the reactor by means of pressure difference (this will be the zero-reaction time).
18. Allow the experiment to run for 9-10 hours.
19. When the experiment is finished, turn off the agitation system, the thermal bath and the electric heating mantle and close the blue valve on the pressurization panel.

6.3.3. Sample analysis

1. Switch on the electric heating mantle about 5-7 minutes before analysis (keep it at minimum power).
2. Turn on the computer, load the online program and select the method.
3. Wait for the program to be “READY”.
4. Check that the nitrogen valve is closed.
5. Open the nitrogen valve on the pressurization panel.
6. Check that the circuit is at atmospheric pressure (via the relief valve).
7. Open the sample valve to fill the sampling area with the mixture contained in the reactor and leave it open for analysis.
8. Wait about 2-3 minutes to ensure that the mixture reaches the injection valve.
9. Press the green arrow on the program.
10. Save the analysis as the experimental conditions and press “OK AND RUN”.
11. Wait for 0.5 minutes (corresponding to the injection time).
12. Close the sample valve.
13. Open the vent valve to reduce the reactor pressure to about 20 bar and then close it.
14. Open the nitrogen valve.
15. Open the sample valve to 25 bars in the reactor and close it.
16. Close the sample valve.
17. Repeat steps 12 and 14 two more times.
18. Open the relief valve to clean the circuit.
19. Once no more liquid comes out of the purge, close the nitrogen valve and wait until the sampling zone is depressurized before closing the relief valve.

6.3.4. Cleaning

1. Depressurize the reactor with the vent valve.
2. Unscrew the sampling circuit from the sample valve.
3. Unscrew the one-way valve.
4. Disassemble the agitation system.
5. Open the reactor.

6. Use a vacuum pump to extract the mixture from inside the reactor.
7. Filter the mixture to separate it from the catalyst and store it (throw the catalyst into the appropriate container).
8. Extract the remaining catalyst from the reactor with acetone.
9. Filter the acetone from the catalyst to deposit it in the corresponding waste drums.
10. Clean the reactor cover with acetone to extract the remains of catalyst.
11. Clean the filter by means of differential pressure (with acetone and pressurised air).
12. Dry the reactor cover and the interior of the reactor with pressurised air to ensure that no substances remain to interfere with the analysis.

6.4. EXPERIMENTAL CONDITION

The experiments carried out lasted between 9 to 10 hours. The process took place under constant pressure and temperature. The operating pressure was always the same (25 bars) to keep the substances in a liquid state. The initial molar ratio of levulinic acid to 1-butene was adjusted to 1 and is defined as:

$$R^0_{LA/1B} = \frac{n^0_{LA}}{n^0_{1B}} \left[\frac{mol}{mol}\right] \tag{32}$$

Four different temperatures were studied to obtain different values of the thermodynamic equilibrium constant and to determine the reaction enthalpy change of the system. The temperatures chosen are those shown in Table 12. To speed up the process, higher quantities of catalyst were used at low temperature.

Temperature [ºC]	**Catalyst** [g]
90	10
100	5
110	5
120	5

Table 12. Amount of catalyst used at the different working temperatures.

To check that the value of the constant did not vary with the initial composition, an experiment was carried out at 100 ºC with a molar ratio of 1.5.

6.4.1. Calibration

To be able to quantify the compounds present in the mixture, a calibration of the chromatograph is necessary to know the relationship between the mass concentrations and the chromatographic areas of the substances. This is done by means of standards of known composition that cover the whole range of possible concentrations in this study. Three replicates of the analysis will be made of each standard in order to evaluate the statistical dispersion.

Due to the pandemic, calibration could not be performed. Therefore, for the calculation of the equilibrium constant, chromatographic areas have been used instead of molar concentrations.

7. EXPERIMENTAL RESULTS AND DISCUSSION

The esterification of levulinic acid with 1-butene using the Amberlyst 15 ion exchange resin as a catalyst gives sec-butyl levulinate as the product. Besides the main one, secondary reactions are formed by isomerization of 1-butene to 2-butene and by hydration of 1-butene and 2-butene to 2-butanol (2-BuOH). Another possible secondary reaction would be the formation of dimers of 1B, but with the starting conditions they have not been detected.

Chromatographic areas will be used instead of concentrations for calculations of the thermodynamic constant since, due to confinement, the experimental work could not be completed. For these values to be considered provisional, it is assumed that all compounds in the experimental system show the same chromatographic response. The areas obtained in the different experiments are shown in Appendix 3.

To check that the values obtained are good, the thermodynamic values of the isomerization of 1-butene to trans-2-butene (trans-2B) are calculated and compared with the theoretical values. The theoretical values are determined using the standard formation enthalpies and entropies of 1-butene and 2-butene that have been found in the literature. The same will be done for the isomerization of trans-2-butene to cis-2-butene (cis-2B).

As the mixture is not ideal, the estimation of the activity coefficients (γ_i) are made by the UNIFAC-Dortmund prediction method. For this, it is necessary to know the molar fractions of the different compounds (x_i). From molar fractions, the activities (a_i) of the different compounds can be estimated. The thermodynamic equilibrium constant for a non-ideal liquid phase system is given by:[44]

$$K_a = \prod_{i=1}^{S} \left(a_i'\right)_e^{v_i} = \prod_{i=1}^{S} \left(\gamma_i\right)_e^{v_i} \cdot \left(x_i\right)_e^{v_i} = \prod_{i=1}^{S} \left(\gamma_i\right)_e^{v_i} \prod_{i=1}^{S} \left(x_i\right)_e^{v_i} = K_\gamma \cdot K_x \qquad (33)$$

${K_\gamma}^n$ was calculated as:

$$ {K_\gamma}^1 = \frac{\gamma_{SBL}}{\gamma_{LA} \cdot \gamma_{1B}} \tag{34} $$

$$ {K_\gamma}^2 = \frac{\gamma_{trans-2B}}{\gamma_{1B}} \tag{35} $$

$$ {K_\gamma}^3 = \frac{\gamma_{cis-2B}}{\gamma_{trans-2B}} \tag{36} $$

${K_x}^n$ was calculated using the molar fractions:

$$ {K_x}^1 = \frac{x_{SBL}}{x_{LA} \cdot x_{1B}} \tag{37} $$

$$ {K_x}^2 = \frac{x_{trans-2B}}{x_{1B}} \tag{38} $$

$$ {K_x}^3 = \frac{x_{cis-2B}}{x_{trans-2B}} \tag{39} $$

The values obtained from K_γ and K_x for the reactions carried out in the system are as follows:

T [K]	x_{1B}	$x_{trans-2B}$	x_{cis-2B}	x_{2BuOH}	x_{LA}	x_{SBL}	${K_x}^1$	${K_x}^1$ average	${K_x}^2$	${K_x}^2$ average	${K_x}^3$	${K_x}^3$ average
363	0.011	0.129	0.064	0.016	0.272	0.508	176	173 ± 33	12.1	11.8 ± 2.3	0.50	0.499 ± 0.001
363	0.011	0.128	0.064	0.016	0.273	0.507	165		11.4		0.50	
373	0.013	0.133	0.067	0.018	0.315	0.454	114	113.3 ± 1.2	10.5	10.48 ± 0.05	0.51	0.509 ± 0.013
373	0.012	0.122	0.063	0.019	0.338	0.446	113		10.5		0.51	
383	0.012	0.111	0.058	0.017	0.410	0.392	82	87 ± 23	9.5	9.5 ± 0.1	0.53	0.527 ± 0.006
383	0.015	0.140	0.073	0.019	0.316	0.438	94		9.5		0.53	
383	0.015	0.139	0.073	0.019	0.336	0.418	85		9.5		0.53	
393	0.017	0.144	0.078	0.019	0.344	0.398	69	65 ± 13	8.6	8.6 ± 0.3	0.54	0.543 ± 0.008
393	0.016	0.137	0.074	0.018	0.368	0.386	66		8.6		0.54	
393	0.008	0.073	0.040	0.014	0.569	0.295	62		8.7		0.55	

Table 13. Molar fractions calculated from chromatographic areas and their constant K_x.

T [K]	γ_{1B}	$\gamma_{trans\text{-}2B}$	$\gamma_{cis\text{-}2B}$	γ_{2BuOH}	γ_{LA}	γ_{SBL}	K_γ^1	K_γ^1 average	K_γ^2	K_γ^2 average	K_γ^3	K_γ^3 average
363	1.09	1.25	1.25	0.88	1.38	0.99	0.66	0.66 ± 0.00	1.15	1.15 ± 0.00	1.00	1.00 ± 0.00
363	1.09	1.25	1.25	0.88	1.38	0.99	0.66		1.15		1.00	
373	1.11	1.28	1.28	0.93	1.34	0.99	0.66	0.67 ± 0.03	1.15	1.15 ± 0.01	1.00	1.00 ± 0.00
373	1.13	1.30	1.30	0.93	1.32	1.00	0.67		1.16		1.00	
383	1.17	1.36	1.36	0.99	1.25	1.02	0.69	0.67 ± 0.06	1.17	1.15 ± 0.03	1.00	1.00 ± 0.00
383	1.11	1.28	1.28	0.96	1.35	0.99	0.66		1.15		1.00	
383	1.12	1.29	1.29	0.97	1.33	0.99	0.66		1.15		1.00	
393	1.13	1.30	1.30	1.01	1.32	0.99	0.66	0.69 ± 0.16	1.15	1.17 ± 0.09	1.00	1.00 ± 0.00
393	1.14	1.32	1.32	1.01	1.30	1.00	0.67		1.15		1.00	
393	1.30	1.55	1.55	1.11	1.14	1.10	0.74		1.19		1.00	

Table 14. Activity coefficients and their constant K_γ.

In Table 14 you can see that the values of K_γ are different from 1. This proves that the medium is not ideal.

As can be seen, the activity coefficients of levulinic acid are higher than those of sec-butyl levulinate. This result is expected because levulinic acid is more polar than the ester. In the case of trans-2B and cis-2B, it has the same value because they have the same molecular formula, but with different three-dimensional orientation.

The Poynting correction factor (K_Γ) has been used to solve the deviation of the K_a values caused by the difference between the working pressure and the standard pressure: [44]

$$K_\Gamma = exp\left(\frac{P-1}{R \cdot T} \cdot \sum_{i=1}^{S} v_i \cdot V_i\right) \tag{40}$$

Where V_i is the molar volume of compound i and R is the gas constant in atm L mol^{-1} K^{-1}. The values of the molar volumes and correction factors are shown in the following tables:

T [K]	V_{1B} [L/mol]	$V_{trans\text{-}2B}$ [L/mol]	$V_{cis\text{-}2B}$ [L/mol]	V_{2BuOH} [L/mol]	V_{LA} [L/mol]	V_{SBL} [L/mol]
363	0.0010	0.0119	0.0059	0.0015	0.0279	0.0898
363	0.0010	0.0119	0.0059	0.0015	0.0279	0.0897
373	0.0012	0.0123	0.0062	0.0016	0.0322	0.0803
373	0.0011	0.0113	0.0058	0.0017	0.0346	0.0789
383	0.0011	0.0102	0.0054	0.0016	0.0420	0.0693
383	0.0014	0.0129	0.0068	0.0017	0.0324	0.0774
383	0.0013	0.0128	0.0068	0.0017	0.0344	0.0740
393	0.0015	0.0133	0.0072	0.0018	0.0353	0.0703
393	0.0015	0.0127	0.0069	0.0017	0.0377	0.0683
393	0.0008	0.0068	0.0037	0.0013	0.0583	0.0522

Table 15. Molar volumes.

T [K]	K_{Γ}^{1}	K_{Γ}^{1} **average**	K_{Γ}^{2}	K_{Γ}^{2} **average**	K_{Γ}^{3}	K_{Γ}^{3} **average**
363	1.05	1.050 ± 0.001	1.01	1.0088 ± 0.0002	0.995	0.995 ± 0.000
363	1.05		1.01		0.995	
373	1.04	1.04 ± 0.01	1.01	1.008 ± 0.002	0.995	0.995± 0.001
373	1.03		1.01		0.996	
383	1.02	1.03 ± 0.02	1.01	1.008 ± 0.004	0.996	0.996 ± 0.002
383	1.03		1.01		0.995	
383	1.03		1.01		0.995	
393	1.03	1.01 ± 0.06	1.01	1.007 ± 0.008	0.995	0.996 ± 0.004
393	1.02		1.01		0.996	
393	0.99		1.00		0.998	

Table 16. Correction factors.

The values from K_{Γ} are similar in the different experiments and close to unity. This means that K_a is only dependent on temperature because the deviation caused by pressure is considered to be negligible.

If the Poynting correction factor is taken into account, the thermodynamic equilibrium constant is rewritten as follows:

$$K_a = K_{\gamma} \cdot K_x \cdot K_{\Gamma} \tag{41}$$

Table 17 shows the average values of the equilibrium constant for each temperature for SBL synthesis.

T [K]	K_x	K_γ	K_Γ	K_a	**Estimated** K_a
363	170	0.66	1.05	118 ± 23	369
373	113	0.67	1.04	78.7 ± 1.8	284
383	87	0.67	1.03	60 ± 13	220
393	65	0.69	1.01	45.9 ± 3.3	172

Table 17. Experimental and estimated equilibrium constants.

The table above shows the non-ideality of the system because K_γ values quite different from 1. This variation is due to the fact that the activity coefficient of the compounds is different from 1. The compounds showing a more non-ideal behaviour are trans-2B, cis-2B, LA and 1B. Compounds that show near-ideal behavior are 2-BuOH and SBL.

If we look at the equilibrium constant, we can see that the estimated values are higher than those obtained experimentally. Due to the confinement, the experimental work could not be completed and the chromatographic areas has been used instead of the concentrations to estimate of K_a experimental values. These results are considered provisional. Furthermore, the theoretical constant is estimated by means of experimental methods with cumulative errors that are reflected in the increase of its value.

As the K_a values are high, it is concluded that the esterification of levulinic acid with 1-butene is mainly displaced to the formation of the product. In addition, a K_a values as a function of temperature decreases with temperature, showing that the esterification reaction is exothermic.

The levulinic acid conversion is calculated to check if they are high. Table 18 shows the averages of LA conversions for the different temperatures and initial conditions.

$R_m{}^{o}{}_{AL/1B}$	**T** [K]	X_{LA}
1	363	0.65
1	373	0.58
1	383	0.54
1	393	0.46
1.5	373	0.36

Table 18. The conversion of LA.

Table 18 shows how the conversion of LA is decreased as the temperature increases. When comparing the conversion with an initial molar ratio of 1 and 1.5 at 100 ºC, it can be seen that a higher conversion is obtained at ratio 1. This justifies the initial molar ratio used in these experiments.

Table 19 shows the values of the thermodynamic constant obtained at 100 ºC but at two different initial molar ratios, at 1 and 1.5. The values obtained are practically the same, which confirms that the thermodynamic equilibrium constant depends only on temperature as expected.

$\mathbf{R^0_{LA/1B}}$	**T** [K]	$\mathbf{K_a}^1$
1	373	78
1	373	79
1.5	373	74

Table 19. Experiments at 100 ºC and a different initial molar ratio.

Using equation 16, the thermodynamic equilibrium constant can be related to the thermodynamic variables of the system. If it is assumed that the enthalpy variation of the reaction is constant in the studied temperature range, when representing the experimental values fitted to equation 16, the standard molar enthalpy change of the reaction ($\Delta_r H^o_{(l)}$) and the standard molar entropy change of the reaction ($\Delta_r S^o_{(l)}$) are obtained from the slope and the intercept, respectively.[44] Figure 6 shows the variation of the thermodynamic equilibrium constant with temperature.

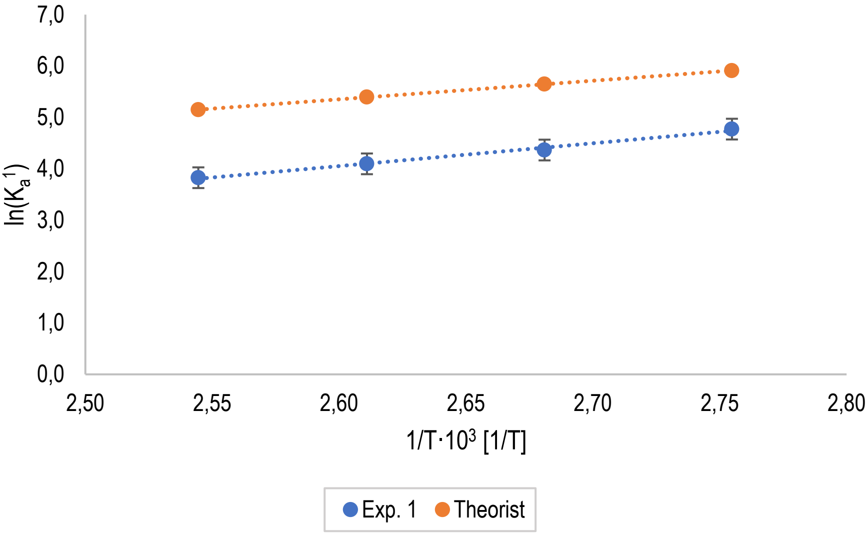


Figure 6. ln(K_a^1) versus 1/T.

The representations show a rising line that confirms that the reaction system is exothermic. If the theoretical and experimental slopes are compared, they are similar. However, the theoretical values are higher probably because of inaccuracy of properties estimation and also because molar fractions of the different species are estimated due to the lack of proper calibration equations. For the estimation of the thermodynamic variables, the linear regression method has been used. Therefore, the dependence of K_a^1 on temperature is described as:

$$\ln(K_a) = (4439 \pm 271) \cdot \frac{1}{T} - (7.49 \pm 0.72) \qquad (42)$$

Table 20 shows the values obtained from $\Delta_r H°_{(l)}$ and $\Delta_r S°_{(l)}$ for the esterification reaction as mentioned above. As can be seen, the value of the enthalpy is negative, which agree with the fact that reaction is exothermic.

$\Delta_r H°_{(l)}$ [kJ/mol]	**$\Delta_r S°_{(l)}$** [J/mol·K]
- 36.9 ± 2.3	- 62.3 ± 6.0

Table 20. Thermodynamic variables values.

The thermodynamic values shown in Table 20 were obtained considering that there was no dependence on temperature. If it is considered that the standard reaction enthalpy changes significantly in the studied temperature range, equation 16 should be reformulated with the expressions 14 and 15 as follows:[44]

$$\ln(K_a) = -\frac{\Delta H_r^o(298.15K) + \int_{298.15K}^{T} \sum_i v_i C_{pL,i}(T)\, dT}{RT} + \frac{\Delta S_r^o(298.15K) + \int_{298.15K}^{T} \frac{\sum_i v_i C_{pL,i}(T)}{T} dT}{R} \quad (43)$$

Rewriting equation 41:

$$\ln(K_a) + f(T) = -\frac{\Delta H_r^o(298.15K)}{RT} + \frac{\Delta S_r^o(298.15K)}{R} \quad (44)$$

By representing K$_a$ values according equation 44, the value of the standard molar enthalpy of the reaction at 298.15 K can be estimated through the slope and the standard molar entropy of the reaction at 298.15 K from the intercept. Figure 7 shows the representation of the theoretical and experimental equilibrium constant against temperature and Table 21 shows the thermodynamic values of the esterification reaction.

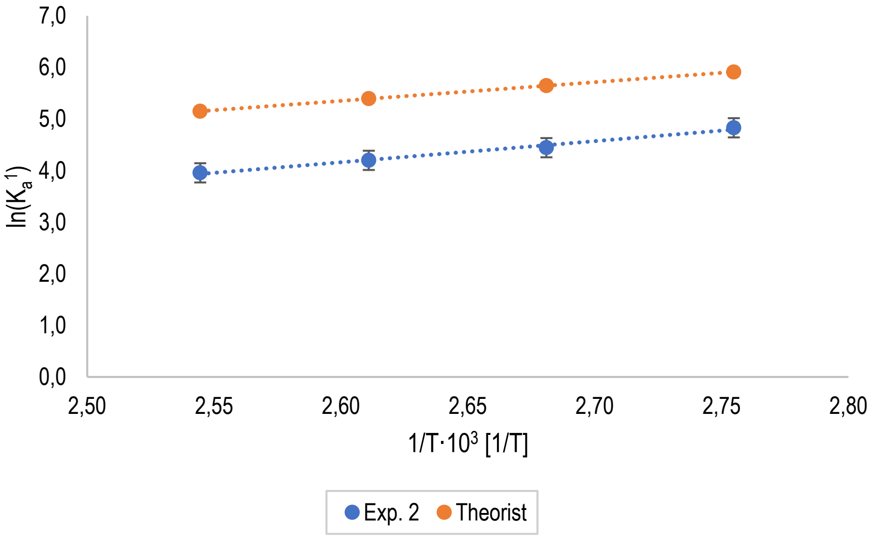


Figure 7. ln(K$_a^1$) + f(T) versus 1/T.

$\Delta_rH^o_{(l)}$ [kJ/mol]	**$\Delta_rS^o_{(l)}$** [J/mol·K]
- 34.1 ± 2.4	- 54.0 ± 6.4

Table 21. Thermodynamic variables values.

The experimental values of standard molar enthalpy and standard molar entropy of the reaction at 298.15 K are given in Table 22 together with the theoretical values obtained in this study.

Studies	**$\Delta_rH^o_{(l)}$** [kJ/mol]	**$\Delta_rS^o_{(l)}$** [J/mol·K]
Theoretical	- 27.3	- 25.5
$\Delta_rH^o_{(l)}$ constant with T	- 36.9 ± 2.3	- 62.3 ± 6.0
$\Delta_rH^o_{(l)}$ changes with T	- 34.1 ± 2.4	- 54.0 ± 6.4

Table 22. Thermodynamic values at 298.15 K obtained in this study.

As can be seen, the value of $\Delta_rH^o_{(l)}$ considering that it is dependent on temperature is lower than the value obtained if this is considered constant in the studied temperature range. This implies that the variation of the standard reaction enthalpy with temperature is quite significant. This fact should be taken into account in the calculations related to a process for obtaining SBL. For example, the evaluation of heating/cooling reaction needs.

To check the quality of experimental values, the experimental and theoretical thermodynamic values of the isomerization of 1-butene to trans-2-butene are compared. For this purpose, it is necessary to calculate the enthalpy and standard entropy of the reaction by means of equations 1 and 4 with the 1-butene and trans-2-butene values from the literature (Table 7). As the thermodynamic values are needed in the range of temperatures studied, equations 14 and 15 will be used together with the expressions of Cp in the liquid state estimated by the "Ruzicka and Domalski method" (Table 3). For the experimental calculation it is assumed that the reaction enthalpy varies with temperature. Table 23 shows the average values of the equilibrium constant for each temperature for the secondary reaction and Table 24 shows the theoretical and experimental thermodynamic values for the isomerization of 1-butene to trans-2-butene. Figure 8 shows the theoretical and experimental equilibrium constant as a function of temperature.

T [K]	K_x	K_γ	K_Γ	K_a	Estimated K_a
363	11.8	1.15	1.009	13.6 ± 2.6	4,66
373	10.48	1.15	1.008	12.2 ± 0.2	4,17
383	9.5	1.15	1.008	11.0 ± 0.2	3,76
393	8.6	1.17	1.007	10.1 ± 1.0	3,41

Table 23. Experimental and estimated equilibrium constants for isomerization of 1B to trans-2B.

Studies	$\Delta_r H^o_{(l)}$ [kJ/mol]	$\Delta_r S^o_{(l)}$ [J/mol·K]
Theoretical	-12.5	-21.7
Experimental	- 11.8 ± 0.3	-10.8 ± 0.7

Table 24. Thermodynamic values at 298.15 K obtained for isomerization of 1B to trans-2B.

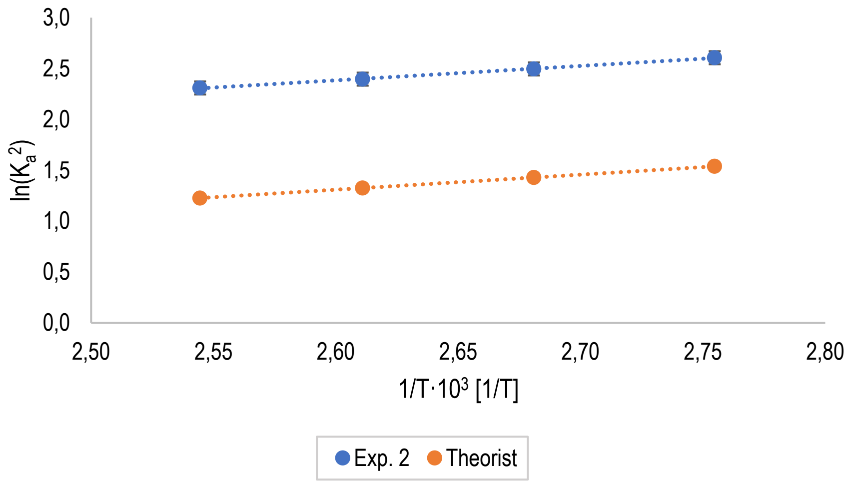


Figure 8. $\ln(K_a^2)$ versus 1/T.

As shown in the table 24, the experimental values of reaction enthalpy are of the same order as those obtained from the literature. It follows that the experimental values, despite they are provisional, seems to be of high quality.

For isomerization of trans-2-butene to cis-2-butene the same procedure is carried out, but assuming that the enthalpy of the reaction is temperature independent. This is because the expression of Cp is the same for both substances. The equilibrium constants obtained for this reaction are shown below.

T [K]	K_x	K_γ	K_Γ	K_a	Estimated K_a
363	0.499	1.000	0.995	0.497 ± 0.001	1.81
373	0.509	1.000	0.995	0.507 ± 0.013	1.87
383	0.527	1.000	0.996	0.525± 0.006	1.92
393	0.543	1.000	0.996	0.541 ± 0.011	1.98

Table 25. Experimental and estimated equilibrium constants for isomerization of trans-2B to cis-2B.

Studies	$\Delta_rH^o_{(l)}$ [kJ/mol]	$\Delta_rS^o_{(l)}$ [J/mol·K]
Theoretical	-3.5	-14.6
Experimental	- 3.40 ± 0.28	-3.52 ± 0.73

Table 26. Thermodynamic values at 298.15 K obtained for isomerization of trans-2B to cis-2B.

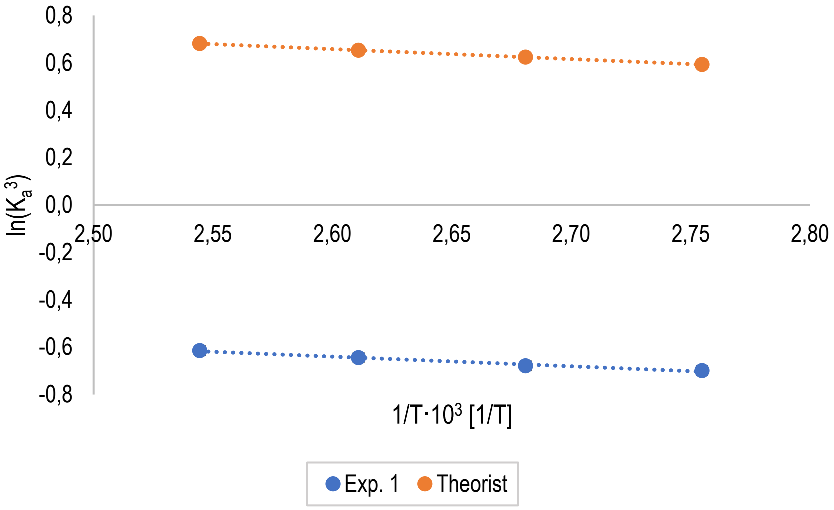


Figure 9. ln(K_a^3) versus 1/T.

As can be seen, the values of the theoretical constant are smaller than those obtained experimentally. This is because the concentrations of trans-2-butene and cis-2-butene are very small. However, the values of the reaction enthalpies are practically the same with which the experimental values can be considered provisional. Taking into account the results obtained with the two isomerization reactions, it can be concluded that the experiments performed are good enough.

To check that the estimated thermodynamic values of the SBL are good enough, these values are calculated from the experimental results and compared with the theoretical ones. The standard values of enthalpy and entropy of the reaction obtained by assuming reaction enthalpy a function of temperature and equations 1 and 4 are used. In Table 27 it is verified that the estimates made can be considered valid since the thermodynamic values are similar and of the same order.

Studies	**$\Delta_f H^o(l,T_o)$** [kJ/mol]	**$S^o(l,T_o)$** [J/mol·K]
Theoretical	-731.9	470.1
Experimental	-738.7	441.6

Table 27. Thermodynamic values of the SBL at 298.15K.

Although it was not possible to complete the experimental program, it has been shown that the results obtained can be considered of high quality and can be used on a provisional basis. Also, it should be noted that the enthalpy values obtained experimentally and theoretically are close to each other. This confirms that the estimates made during the calculation of the thermodynamic values of the SBL are good enough.

RECOMMENDATIONS

Following this study, the real values of the equilibrium constant and the thermodynamic magnitudes should be obtained. This would require calibration of the chromatograph with mixtures of known concentrations. Once the real values are obtained, the reaction rate of the esterification of levulinic acid with 1-butene should be determined using an ion exchange resin of type A15 as a catalyst. The process would go from the beginning of the experiment until chemical equilibrium was reached and would involve the determination of the reaction rate at different compositions, which would be obtained by sampling at different times.

8. CONCLUSIONS

1. Reaction enthalpies found experimentally for isomerization reactions of 1-butene to trans-2-butene, and cis-2-butene to trans-2-butene are practically the same that the ones estimated theoretically. This fact proves that obtained experimental values for SBL formation are good enough despite they can be considered preliminary since it was no possible to complete the experimental program.
2. As the K_a values of the reaction of SBL formation are high, it is concluded that the equilibrium is mainly shifted towards the products.
3. The reaction of SBL formation is exothermic as Ka variation with temperature shows.
4. The experimental value of the standard enthalpy of the reaction at 25 ºC is similar to the value obtained theoretically.
5. For the esterification reaction, it is shown that the standard enthalpy of the reaction varies significantly with temperature.
6. The theoretical estimations of the thermodynamic values of sec-butyl levulinate are valid because they are similar to those obtained by experiments. This fact suggests that the methods used provide good values for the thermodynamic properties of the esters.

9. RECOMMENDATIONS

Following this study, the real values of the equilibrium constant and the thermodynamic magnitudes should be obtained. This would require calibration of the chromatograph with mixtures of known concentrations. Once the real values are obtained, the reaction rate of the esterification of levulinic acid with 1-butene should be determined using an ion exchange resin of type A15 as a catalyst. The process would go from the beginning of the experiment until chemical equilibrium was reached and would involve the determination of the reaction rate at different compositions, which would be obtained by sampling at different times.

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11. ACRONYMS

a_i	Activity
γ_i	Activity coefficient
A15	Amberlyst 15
T_b	Boiling temperature
2-BuOH	2-Butanol
1B	1-Butene
BL	Butyl levulinate
cis-2B	cis-2-Butene
CS	Conventional sulfonation
P_c	Critical pressure
T_c	Critical temperature
DVB	Divinylbenzene
EL	Ethyl levulinate
FA	Formic acid
Cp	Heat capacity
HMF	Hydroxymethylfurfural
LA	Levulinic acid
OS	Over sulfonation
SBL	sec-Butyl levulinate
S^o	Standard entropy of compound
ΔH_f^o	Standard formation enthalpy
ΔH_r^o	Standard reaction enthalpy
ΔS_r^o	Standard reaction entropy
T	Temperature
K_a	Thermodynamic equilibrium constant
trans-2B	trans-2-Butene

APPENDICES

APPENDIX 1: CHROMATOGRAPHIC METHOD

Valves					
Injection valve	Type:	Gas Sampling Valve			
	Loop volume:	0.2 µL			
	Load time:	0.5 min			
	Inject time:	0.5 min			
Valve box	Heater:	150 ºC			
Inlets: Front SS inlet He					
Mode: Split	Heater:	250 ºC			
	Pressure:	1.1402 bars			
	Total flow:	228.5 mL/min			
	Septum purge flow:	3 mL/min			
	Gas saver:	20 mL/min after 2 min			
Split ratio:	450:1	Split flow:	225 mL/min		
Column					
Temperature Range:	-60 ºC – 325 ºC (350 ºC)				
In:	Front SS Inlet He				
On:	MSD				
Control Mode: Constant flow	Initial temperature:	40 ºC			
	Pressure:	1.1402 bars			
	Flow:	0.5 mL/min			
	Average Velocity:	19.861 cm/sec			
	Holdup time:	4.1957 min			
Post run:	1 mL/min				
Oven					
Oven temperature:	40 ºC	Equilibration time:	0 min	Max temperature:	325 ºC
	Rate	Value	Hold time	Run time	
Initial	-	40 ºC	5 min	5 min	
Ramp 1	35 ºC/min	200 ºC	9 min	18.571 min	
Post run time:	50 ºC	Post run:	0 min		
Thermal Aux 2 (MSD transfer line)					
Initial temperature:	280 ºC				

APPENDIX 2: ESTIMATION OF THE THEORETICAL CONSTANT

Compound	Groups	n_i	a_i	b_i	d_i
LA	C - (3H,C)	1	3.8452	-0.33997	0.19489
	CO - (2C)	1	5.4375	0.72091	-0.18312
	C - (2H,2C)	2	2.7972	-0.054967	0.10679
	CO - (C,O)	1	29.246	3.4261	-2.8962
	O - (H,C)	1	12.952	-10.145	2.6261
1B	C - (3H,C)	1	3.8452	-0.33997	0.19489
	C - (2H,2C)	1	2.7972	-0.054967	0.10679
	= C - (H,C)	1	4.0749	-1.0735	0.21413
	= C - (2H)	1	4.1763	-0.47392	0.099928
SBL	C - (3H,C)	3	3.8452	-0.33997	0.19489
	C - (2H,2C)	3	2.7972	-0.054967	0.10679
	C - (H,2C,O) (ether)	1	0.9879	0.39403	-0.01612
	O - (2C)	1	5.0312	-1.5718	0.3786
	CO - (C,O)	1	29.246	3.4261	-2.8962
trans-2B/ cis-2B	C - (3H,C)	2	3.8452	-0.33997	0.19489
	= C - (H,C)	2	4.0749	-1.0735	0.21413

Table A. The contribution of the groups presents in LA, 1B, SBL, trans-2B and cis-2B (Ruzicka and Domalski method).[40]

Groups	N_k	Δhfk
CH_3 (1)	3	-76.45
CH_2 (2)	3	-20.64
CH (3)	1	29.89
C = O (2)	1	-133.22
COO (2)	1	-337.92

Table B. Tabulated values of Δhfk (Joback method).[40]

Groups	N_k	tbk	tck	pck
CH_3 (1)	3	23.58	0.0141	-0.0012
CH_2 (2)	3	22.88	0.0189	0
CH (3)	1	21.74	0.0164	0.002
C = O (2)	1	76.75	0.038	0.0031
COO (2)	1	81.1	0.0481	0.0005

Table C. Tabulated values of tbk, tck and pck (Joback method).[40]

Groups	N_k	S_k^o
CH3 - (C)	2	127.29
CH2 - (2C)	1	39.43
CH - (2C,O)	1	-46.04
O - (C,CO)	1	35.12
CH2 - (C,CO)	2	40.18
CH3 - (CO)	1	127.29

Table D. Tabulated values of S_k^o (Benson method).[40]

Groups	N_k	CpAk	CpBk	CpCk	CpDk
CH3 (1)	3	19.5	-8.08E-03	1.53E-04	-9.67E-08
CH2 (2)	3	-0.909	9.50E-02	-5.44E-05	1.19E-08
CH (3)	1	-23	2.04E-01	-2.65E-04	1.20E-07
C = O (2)	1	6.45	6.70E-02	-3.57E-05	2.86E-09
COO (2)	1	24.5	4.02E-02	4.02E-05	-4.52E-08

Table E. Tabulated values of CpAk, CpBk, CpCk y CpDk (Joback method).[40]

APPENDIX 3: EXPERIMENTAL VALUES

$R^0_{LA/1B}$	**T** [K]	A_{1B}	$A_{trans\text{-}2B}$	$A_{cis\text{-}2B}$	A_{2BuOH}	A_{LA}	A_{SBL}	A_{TOTAL}
1	363	8005568	92108563	46187347	16330338	314220846	1144767814	1621620476
	363	7684956	93111839	46478735	15241474	407710496	1127996539	1698224039
	373	9696821	101582928	51546406	18110819	497409241	1064864307	1743210522
	373	9414355	98771551	50524408	20287849	565514934	1107241239	1851754336
	383	10219157	96629856	50984026	19641910	739042412	1049204238	1965721599
	383	10830717	102748450	53976482	18103364	481760299	988517515	1655936827
	383	12282739	116968601	61820391	21106073	585404639	1081059776	1878642219
	393	12658630	108872026	58994389	19355668	539579805	924000680	1663461198
	393	12487243	107290288	58022734	18929965	594690257	926672624	1718093111
	393	7996116	69883129	38103919	17789769	1120910079	861927869	2116610881
1.5	373	5525079	55512919	28405662	19659262	1116479737	951007985	2176590644
		Retention time [min]						
		4.952	5.118	5.263	7.661	12.591	13.831	